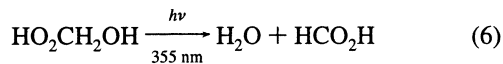


H<sub>2</sub>O<sub>2</sub> than with H<sub>2</sub>O or lattice OH groups, consistent with the finding that HO<sub>2</sub>CH<sub>2</sub>OH is formed at the exclusion of CH<sub>2</sub>(OH)<sub>2</sub> and POCH<sub>2</sub>OH (Figure 5a). In contrast to the behavior of CH<sub>2</sub>(OH)<sub>2</sub> or POCH<sub>2</sub>OH, brief irradiation at 355 nm of FAPO-5 containing HO<sub>2</sub>CH<sub>2</sub>OH (5 min at 500 mW cm<sup>-2</sup>) led to quantitative conversion of the hydroperoxide to HCO<sub>2</sub>H (1677 cm<sup>-1</sup>) and HCO<sub>2</sub><sup>-</sup>⋯Fe (1618 and 2912 cm<sup>-1</sup>), as can be seen from Figure 5, trace b. The 1618 cm<sup>-1</sup> absorption is presumably an overlap of formate and H<sub>2</sub>O product bands:



The simultaneous depletion at 1456, 2884, and 2948 cm<sup>-1</sup> confirms the assignment of these bands to HO<sub>2</sub>CH<sub>2</sub>OH. In a more detailed study, we found that irradiation at 500 mW cm<sup>-2</sup> for a mere 20 s led to complete depletion of HO<sub>2</sub>CH<sub>2</sub>OH. No bleach of CH<sub>2</sub>(OH)<sub>2</sub>, POCH<sub>2</sub>OH, or CH<sub>3</sub>OCH<sub>2</sub>OH was detected under these photolysis conditions. Reaction 6 is the established UV photodissociation channel of hydroxymethylhydroperoxide.<sup>20</sup> Similar loading experiments with CD<sub>2</sub>=O revealed HO<sub>2</sub>-CD<sub>2</sub>OH product absorptions at 2104 and 2256 cm<sup>-1</sup>. As in the case of the parent isotope, reaction with H<sub>2</sub>O<sub>2</sub> was complete on the time scale of an FT-IR run, and subsequent photolysis resulted in efficient conversion to DCO<sub>2</sub>H (1658 cm<sup>-1</sup>) and DCO<sub>2</sub><sup>-</sup>⋯Fe (1613 and 2188 cm<sup>-1</sup>). We conclude that formaldehyde reacts with H<sub>2</sub>O<sub>2</sub> in a FAPO-5 sieve within less than 2 min to yield hydroxymethylhydroperoxide. The adduct rearranges thermally at room temperature to formic acid (formate) and H<sub>2</sub>O with a decay time of about 20 min. Efficient dissociation to the same products takes place upon 355 nm irradiation.

**Implications for a Mechanism of CH<sub>3</sub>OH + O<sub>2</sub> Photooxidation.** The lack of any build-up of the postulated CH<sub>2</sub>=O intermediate upon 355 nm induced reaction of CH<sub>3</sub>OH with O<sub>2</sub> in a FAPO-5 sieve<sup>1</sup> might be due to rapid formation of adducts with CH<sub>3</sub>OH, H<sub>2</sub>O, lattice OH groups, or H<sub>2</sub>O<sub>2</sub>. The considerable stability of CH<sub>3</sub>OCH<sub>2</sub>OH (10 h), CH<sub>2</sub>(OH)<sub>2</sub> (2 h), and POCH<sub>2</sub>OH (2 h) with respect to thermal release of formaldehyde (and subsequent Cannizzaro or Tishchenko reaction) in the room-temperature sieve rules out any significant role of these intermediates. On the other hand, HO<sub>2</sub>CH<sub>2</sub>OH exhibits a much shorter lifetime at room temperature (complete dissociation in 20 min) and is extremely photolabile with respect to fragmentation to HCO<sub>2</sub>H and H<sub>2</sub>O. Clearly, the adduct of formaldehyde and H<sub>2</sub>O<sub>2</sub> might play a role as an intermediate of the CH<sub>3</sub>OH + O<sub>2</sub> photoreaction in FAPO-5 sieve. Time-resolved FT-IR spectroscopy is required to investigate this possibility.<sup>21</sup>

#### IV. Conclusions

In this paper, we have studied the reactivity of gaseous formaldehyde in the pores of an Fe aluminophosphate sieve (AFI

structure) with H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OH, or lattice OH groups. These molecules are present in the reaction mixture of LMCT-induced CH<sub>3</sub>OH + O<sub>2</sub> photooxidation in a FAPO-5 sieve and could therefore act as chemical traps of formaldehyde, a proposed intermediate. Infrared spectra of all four addition products, namely, CH<sub>2</sub>(OH)<sub>2</sub>, HO<sub>2</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OCH<sub>2</sub>OH, and POCH<sub>2</sub>OH, as well as partially deuterated modifications have been established. Knowledge of infrared absorptions of these species is crucial for analyzing mechanistic experiments based on time-resolved FT-IR spectroscopy of CH<sub>3</sub>OH + O<sub>2</sub> photooxidation in this framework substituted transition metal sieve. Among the formaldehyde reaction products, hydroxymethylhydroperoxide, the adduct of CH<sub>2</sub>=O and H<sub>2</sub>O<sub>2</sub>, exhibits thermal and photodissociation behavior consistent with a role in the LMCT-induced photoreaction of CH<sub>3</sub>OH and O<sub>2</sub> in an Fe aluminophosphate sieve.

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